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We have synthesized hcp-Co fine particles with the average diameter of less than 50 nm by sputtering Co in a somewhat high inert gas pressure. A nearly perfect hcp phase can be stabilized by increasing sputtering gas pressure and decreasing sputtering power in contrast to conventional preparation conditions. Magnetic measurements have revealed the clear relation of coercivity with the volume ratio of hcp phase. That is, the increase in the hcp phase considerably enhances the coercivity. Appearance of the hcp phase seems to be related to the promotion of allotropic phase transformation in Co initiated by lattice defects within each particle. © *1997 American Institute of Physics.* [S0021-8979(97)02204-4]

I. INTRODUCTION

Since the pioneering work by Kubo,[1] much attention has been paid to various fine particle systems which exhibit peculiar behaviors quite different from those of bulk samples due to the quantum size effect. Magnetic properties are also significantly influenced by the particle size and shape. In addition to the well-known classical size effects,[2,3] recent experiments have revealed the importance of magnetic quantum tunneling effect in nanometer-scale magnets.[4,5] Thus, magnetic properties of a very fine particle may be quite different from that of a bulk magnet.[6] In these studies, Fe, Ni, γ–Fe_2O_3 and amorphous Co fine particles have been used to study the magnetic properties of fine particles. However, since these materials possess low magnetocrystalline anisotropy, the spin configuration within each nanometer-scale magnet may not be so simple as that of the so-called single-domain particles, causing the analysis of experimental data to be very difficult. If it becomes possible to prepare fine particles with high uniaxial anisotropy, their simple spin structures currently viewed as a two-level system will promote our general understanding of intrinsic behaviors of very small magnets. We consider that hcp Co and its alloy particles, which have large uniaxial magnetocrystalline anisotropy, are one of the most suitable systems for study of the magnetic properties of very small magnets. Although bulk hcp Co is stable below the allotropic transformation temperature of about 420 °C, fcc-phase fine particles are usually stable at ambient temperature.[7–11] Therefore, most attempts have failed in preparing the hcp-Co fine particles. The aim of the present study is to synthesize hcp-Co fine particles and investigate their magnetic properties.

II. EXPERIMENTAL PROCEDURES

Fine Co powders were prepared on a surface oxidized Si(100) at ambient temperature in a home-made dc magnetron sputtering system, with a base pressure less than 1×10^{-7} Torr and an argon gas pressure of 0.1–0.4 Torr. The details of the sputtering apparatus and the sputtering conditions were described elsewhere.[12,13] The magnetic properties were measured by a vibrating sample magnetometer with maximum external field of 10 kOe. Particle size and shape were checked by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The crystal structures of the Co particles were examined by means of x-ray diffraction (XRD) with Cu-Kα line and electron diffraction. In these diffraction experiments, no distinct diffractions other than those from hcp (α)- and fcc (β)-Co were found in all samples prepared in the present study. The rocking curve measurements of $\alpha(10\cdot0)$, $(00\cdot2)$, $(10\cdot1)$, and $\beta(111)$, (200) have revealed that the deposited Co powder samples have no preferential crystallographic orientation, indicating that each powder sample consists of randomly oriented particles. For random orientation, integrated diffraction intensity is given by

$$I = C\left(\frac{1}{v^2}\right)\left[\left|F\right|^2 p\left(\frac{1+\cos^2 2\theta}{\sin^2\theta\,\cos\,\theta}\right)\right]\left(\frac{e^{-2M}}{2\mu}\right), \tag{1}$$

where C is a constant determined by measurement conditions, v the volume of a unit cell, $|F|$ the structure factor, p the multiplicity factor, θ the Bragg angle, e^{-2M} the Debye temperature factor, and μ the linear absorption coefficient.[14] For the mixtures of α and β phases, the diffraction intensity can be simply expressed as

$$I_{\mathrm{mix}}(\theta) = \sum_{\alpha,\beta} c_i I_i(\theta), \tag{2}$$

where c_i and I_i are the volume fraction and the diffraction intensity. Using Eqs. (1) and (2), we can calculate relative intensity ratios of all diffractions from both α and β phases as a function of the volume fractions. It was found that the relative intensities calculated by the above equations can be well fitted to all experimental data by varying the volume fraction of α phase (c_α). Thus, we can determine the volume ratio of α to β phases as $V(\alpha/\beta) = c_\alpha/c_\beta = c_\alpha/(1-c_\alpha)$. The fitting procedures were performed for $\alpha(10\cdot0)$, $(00\cdot2)$, $(10\cdot1)$, and $\beta(111)$, (200).

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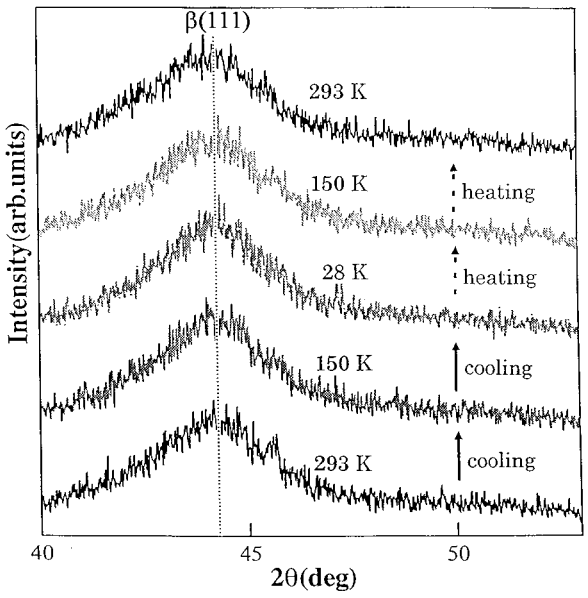

FIG. 1. Variation of the XRD profiles of the β-Co particles grown at an argon gas pressure of 0.15 Torr as a function of temperature. The samples were first cooled down to 28 K and then returned to ambient temperature. It is noticed that the $\beta \rightarrow \alpha$ transition is entirely inhibited in the whole temperature range examined.

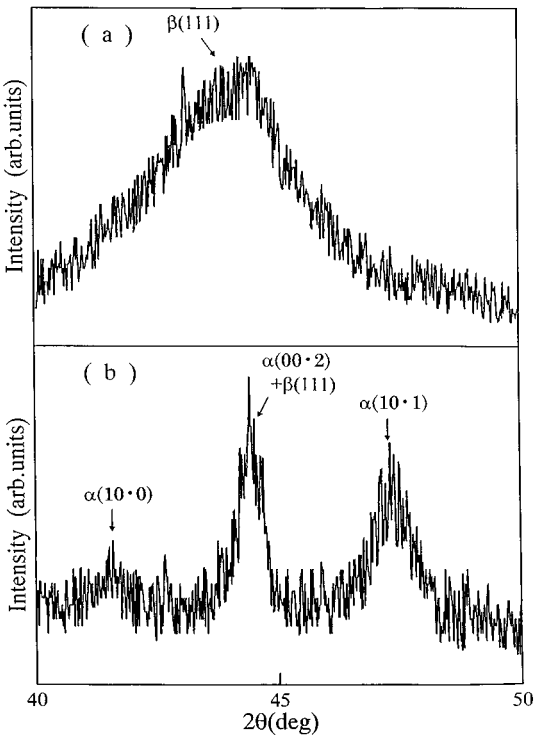

FIG. 2. XRD profiles of the Co particles grown at (a) $P_{Ar}=0.15$ Torr, $I=60$ W and (b) $P_{Ar}=0.35$ Torr, $I=20$ W.

III. RESULTS AND DISCUSSION

A. Inhibition of fcc-hcp transformation

In the thermal equilibrium state, bulk Co is transformed at about 420 °C from the high temperature fcc phase (β) to the low temperature hcp phase (α). However, the phase transformation of fine Co particles on cooling ($\beta \rightarrow \alpha$) is considerably suppressed.[7–11] The effect of the particle size on the transformation is not fully understood although some qualitative discussions were given.[7,15] We recently reported that Co particles prepared by the sputtering method had also pure β phase, and subsequent annealing above the bulk β-α transformation temperature and slow cooling to ambient temperature experiments demonstrated that no phase change was observed in the β-Co particles.[16] This means that the high temperature β phase was not simply produced by rapid cooling in condensation process of metal vapor. This β phase is also found to be very stable even at very low temperatures. As seen in the XRD profiles as a function of temperature (Fig. 1), the $\beta \rightarrow \alpha$ phase transformation in the β-Co particles with a diameter of 10 nm is entirely inhibited down to 28 K. The cause for such a drastic decrease in the transformation temperature will be qualitatively discussed later. In the temperature range of 28–293 K, the thermal expansion effect will shift the $\beta(111)$ peak by utmost 0.02 deg, which is too small to detect the shift due to the broadness of the (111) peak.

B. Formation of α-Co particles

In the present study, we have attempted to synthesize α-Co particles by widely changing preparation conditions. Both the sputtering gas pressure (P_{Ar}) and the sputtering power (I) were found to significantly influence the crystal structure and the size distribution of the Co particles. The volume ratio of α- to β-phase is remarkably increased by increasing the argon gas pressure and decreasing the sputtering power. Typical XRD profiles are shown in Fig. 2. When the particles are formed at low gas pressure and high power ($P_{Ar}=0.15$ Torr, $I=60$ W), the crystal structure is pure β. In contrast, with increasing the pressure and decreasing the power ($P_{Ar}=0.35$ Torr, $I=20$ W), the diffraction peaks (10·0) and (10·1) peculiar to α-Co can be clearly observed. The same results were also confirmed by electron diffraction experiments. Figure 3 illustrates how the gas pressure and the sputtering power affect the crystal structure of Co fine particles. It is clearly noticed that nearly pure α phase is realized for the particles grown at high argon gas pressure and low sputtering power. The particle growth conditions

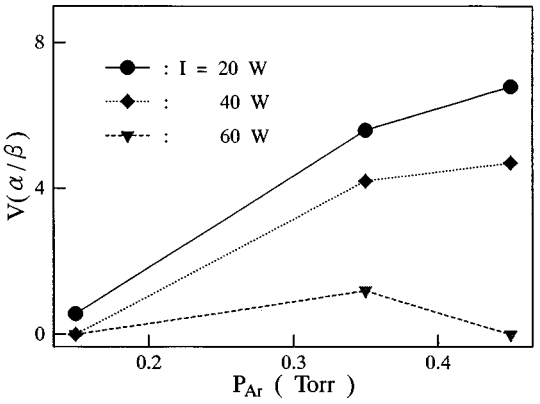

FIG. 3. The influence of the sputtering gas pressure (P_{Ar}) on the volume ratio $V(\alpha/\beta)$ of Co particles for various sputtering power (I).

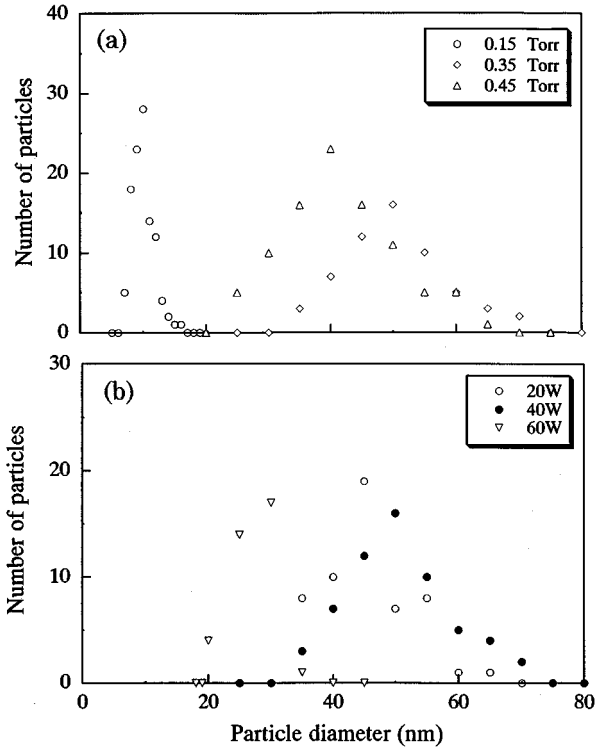

FIG. 4. Size distributions of Co particles measured by TEM: (a) sputtering power $I=20$ W (constant) and (b) sputtering pressure $P_{\mathrm{Ar}}=0.35$ Torr (constant).

also greatly affect the size distribution. Figures 4 and 5 show the size distributions and the typical TEM micrographs of Co particles, respectively. According to these results, the particle size first increases abruptly with increasing the Ar gas pressure from 0.15 to 0.35 Torr, and then tends to saturate. The small Co particles grown at $P_{\mathrm{Ar}}=0.15$ Torr look almost spherical [Fig. 5(a)]. For larger particles grown at $P_{\mathrm{Ar}}\geqslant 0.35$ Torr, however, the pictures are quite different and distinct crystal habit can be seen as evidenced by Figs. 5(b) and 5(c). In order to explain these external shapes of α-Co particles by the Gibbs–Wulff relation,[17] we are trying to determine the crystallographic orientation of each particle by the selected area diffraction method.

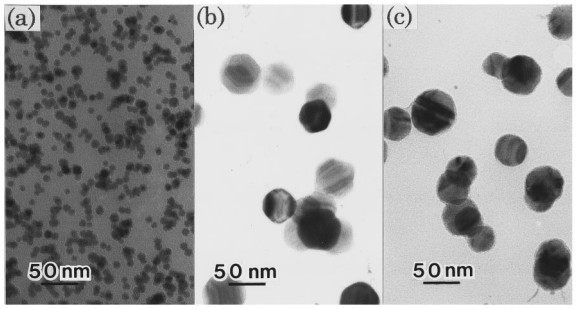

FIG. 5. Bright field images of the Co particles grown at the gas pressures of (a) $P_{\mathrm{Ar}}=0.15$, (b) 0.35, and (c) 0.45 Torr. The sputtering power was $I=20$ W.

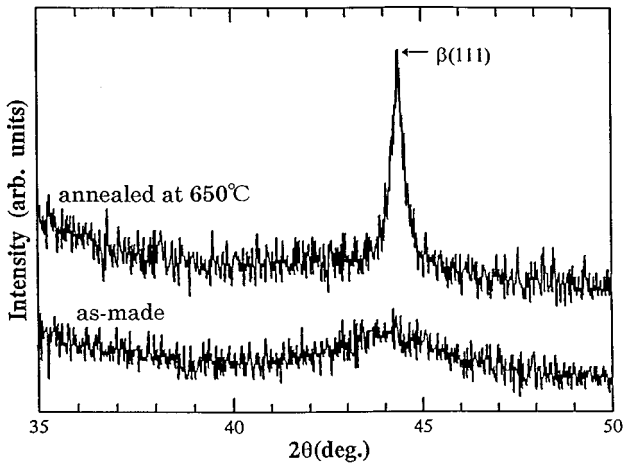

FIG. 6. XRD profiles of the Co particles before and after annealing at 650 °C for 15 h.

C. Phase transformation of Co particles

As mentioned in the previous section, the crystal structure of Co fine particles seems to be closely related to their size. According to Edwards and Lipson,[7] the increase in surface energy due to the transformation may be one of the factors inhibiting the transformation of fine Co particles. The total free energy of a fine particle can be expressed as $G_{iT}=G_{ib}\times v+\gamma_i\times s\ \ (i=\alpha,\beta)$, where G_{ib} is the free energy of bulk, v the particle volume, γ_i the surface energy density, and s the surface area of the particle. Hence, the total free energy difference between α and β particles is given by

$$\Delta G_{\beta-\alpha}=G_{\beta T}-G_{\alpha T}=(G_{\beta b}-G_{\alpha b})v-(\gamma_\alpha-\gamma_\beta)s. \quad (3)$$

The term $(G_{\beta b}-G_{\alpha b})$is an order of 10^6 J/m^3,[18] and the surface energy densities of α and β phases are theoretically calculated to be 2.79 J/m^2 for $\alpha(00\cdot1)$ and 2.73 J/m^2 for $\beta(111)$ by means of a spin-polarized Green's function method,[19] which agree with experiments[20] and the thermodynamically estimated values.[21] Assuming that the particle surface is completely surrounded by the lowest energy crystal planes, that is, (111) for β phase and $(00\cdot1)$ for α phase, both the two terms in Eq. (3) become almost order of 10^{-16}–10^{-18} J when the particle radius is about 10 nm. The surface energy term in Eq. (3) is therefore large enough to reduce the driving force $(\Delta G_{\beta-\alpha})$ of the allotropic transformation of Co, resulting in inhibition of the $\beta\rightarrow\alpha$ transformation in very fine particles. In addition to the above surface effect, the phase transformation might be also influenced by other factors. Figure 6 show the XRD profile of the Co particles annealed at 650 °C for 15.5 h in a hydrogen gas atmosphere and then slowly cooled to ambient temperature. The crystal structure becomes pure β in spite of the very large particle diameter of above 200 nm due to the enhanced grain growth. These results indicate that the crystal structure of Co fine particles is not solely determined by the particle size.

The fcc→hcp transformation is a displacement of the fcc lattice in each second nearest $(111)_{\mathrm{fcc}}$ plane by an amount of

$a/\sqrt{6}$ (a:lattice constant) in $[\bar{1}21]$, $[\bar{2}11]$, and $[11\bar{2}]$ directions, and satisfies the following Shoji–Nishiyama relation[22,23]

$$(111)_{\mathrm{fcc}}//(00\cdot 1)_{\mathrm{hcp}},\ [\bar{2}11]_{\mathrm{fcc}}//[1\bar{1}\cdot 0]_{\mathrm{hcp}}.$$

In spite of numerous studies, the mechanism of the martensitic β-α transformation of Co is not fully understood. Shapiro and Moss[24] proposed a model for the $\beta\rightarrow\alpha$ transition via displacive soft modes in the cubic Γ-L direction which is equivalent to the hexagonal Γ-A direction. However, Frey *et al.*[25] did not find any lattice softening during the β-α transition of Co, and they supported the Seeger's pole dislocation model.[26] According to this model, the β-α transition of Co proceeds through the alternative motion of Shockley type half dislocations with the Bergers vectors of $a/6[121]_\beta$, $a/6[211]_\beta$, and $a/6[112]_\beta$ in the (111) plane of an fcc structure.[26,27] Although the behavior of the dislocations in the Co fine particles is not clarified yet, the following mechanism seems to be plausible. Based on the experimental results on epitaxially grown Co thin films, Grunbaum and Kremer reported that the $\beta\rightarrow\alpha$ phase transformation was mediated by dislocations and stacking faults introduced during the coalescence of deposited small islands.[28] The similar mechanism may occur in the present fine particle system, because the particle growth generally proceeds through the liquidlike coalescence of very fine particles.[29] Thus, the larger particle grown by multiple coalescences may contain more lattice defects, which may act as nucleation sites of the $\beta\rightarrow\alpha$ transformation in the Co fine particles. As mentioned above, we consider that lattice defects, such as dislocations and stacking faults, as well as the particle size affect the martensitic β-α transformation of Co fine particles. It is, however, uncertain whether very slight oxidation of the particle surfaces will affect the transformation or not. According to our experiments, we can at least say that long time exposure of Co particles (less than one week) to the atmosphere does not cause any drastic changes in their XRD profiles.[30] In order to quantitatively understand the transformation mechanism of Co fine particles, more intensive structural investigations are required.

D. Magnetic properties of Co fine particles

Figure 7 shows the coercive force of Co particles as a function of volume ratio $V(\alpha/\beta)$. In the inset, the typical magnetization curve of the nearly perfect α-Co powder $[V(\alpha/\beta)=13]$ is also shown. It should be noted that the coercive force greatly increases as the volume ratio of the α-phase increases, and the maximum value obtained in the present study goes beyond 1400 Oe at $V(\alpha/\beta)=13$. The coherent rotation model predicts $Mr/Ms=0.5$ and $Hc(0)=0.958(K_r+K_2)/Ms$ for a random assembly of noninteracting uniaxial particles,[31] where $Hc(0)$, Mr, Ms, K_1, and K_2, respectively, denote the coercive force, the residual magnetization, the saturation magnetization, and the anisotropy constants. Here, $Hc(0)$ is calculated to be 4000 Oe using the anisotropy constants of bulk hcp-Co.[32] If the magnetostatic interactions among the single-domain particles are taken into account, the coercive force will reduce to $Hc(p)=Hc(0)-pCMs$, here p is the packing fraction, and the coefficient C is 1.7 for randomly packed particles.[33] Since the packing fraction of the present sample is about 0.6, the coercive force of hcp-Co particles should be 2600 Oe, being somewhat larger than the maximum experimental value (1400 Oe). The smaller coercive force is not due to the thermal agitation of spins within each particle, because the thermal energy is very small compared with the magnetic anisotropy energy of hcp-Co particles. Assuming the thermal relaxation time of spins to be 100 s, the coercive force will decrease as $Hc(T)=2K/M_s\ \{1-(25kT/Kv)^{1/2}\}$,[34] where K is the anisotropy constant, k the Boltzmann constant, and v the particle volume. When the particle diameter is about 40 nm as shown in Figs. 5(b) and 5(c), the decrease in the coercive force due to the thermal agitation of spins is estimated to be less than 10%. Therefore, the large discrepancy between the experiments and the theoretical value suggests that the coherent rotation model seems to be inappropriate to describe the magnetic behaviors of the hcp-Co particles. Some authors have already reported about the spin structures of an α-Co particle.[35,36] However, to our knowledge, the full magnetization curve has never been calculated in detail.[35] We hope that the magnetic behaviors of an α-Co particle and the random assembly will be calculated by rigorous micromagnetic simulations. One may think that the exchange interaction between the particle's metallic core and its oxide shell (Co-oxide) might affect the magnetic behaviors. We believe that this effect is very trivial, because the Neel temperature of Co-oxide is lower than room temperature.

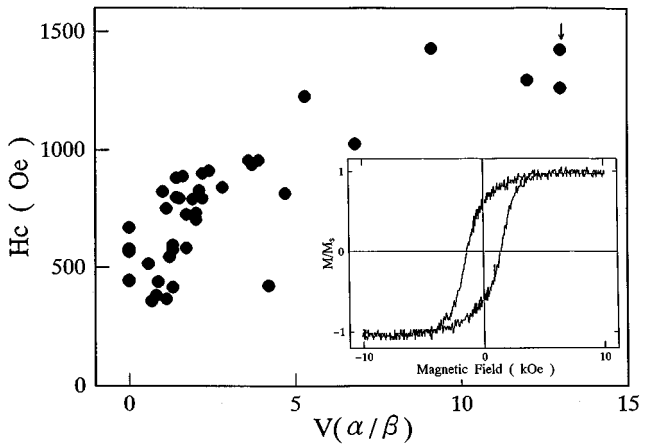

FIG. 7. The coercive force of Co particles as a function of volume ratio $V(\alpha/\beta)$. Inset: the typical magnetization curves of the Co particles with $V(\alpha/\beta)=13$.

IV. SUMMARY

We found that stable hcp-Co fine particles are grown by a sputtering method in a somewhat high gas pressure. Magnetic measurements revealed that the increase in the volume ratio of hcp (α) to fcc (β) phase enhances the coercive force, and the maximum value exceeds 1400 Oe. The $\beta\rightarrow\alpha$ phase transformation was considered to be governed by both the particle size and lattice defects such as dislocations and stacking faults.

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